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364 36Y 373 37Y 591 601
613 624 62X 634 644 652
662 682 694 697 699 805
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(56) Documents cited
GB 1308183
GB 995313
GB 958631
(58) Field of search
C2C
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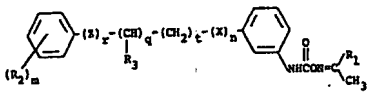
Katsuzo Kamoshita
(74) Agents
Boult, Wade & Tennant

(54) Oximecarbamate derivatives and their use as herbicides

(57) Oximecarbamate derivatives of the formula:



wherein R_1 is methyl or methoxy, R_2 is lower alkyl, lower alkoxy, methylenedioxy, methylthio, halogen or trifluoromethyl, R_3 is hydrogen, methyl or ethyl, X and Z are each oxygen or sulfur, m is an integer from 0 to 5 when R_2 is fluorine or an integer from 0 to 3 when R_2 is other than fluorine when m is 2 or 3, each R_2 is the same as or different from any other R^2, n and r are each 0 or 1 but are not both zero simultaneously, q is 0 or 1 and t is an integer from 0 to 4, which are useful as selective herbicides.

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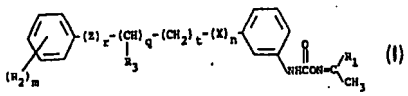
SPECIFICATION

Oximecarbamate derivatives and their use as herbicides

The present invention relates to oximecarbamate derivatives, and their production and use. More particularly, it relates to oximecarbamate derivatives of the formula:



(I)

wherein R_1 is methyl or methoxy, R_2 is lower alkyl, lower alkoxy, methylenedioxy, methylthio, halogen or trifluoromethyl, R_3 is hydrogen, methyl or ethyl, X and Z are each oxygen or sulfur, m is an integer from 0 to 5 when R_2 is fluorine or an integer from 0 to 3 when R_2 is other than fluorine, and when m is 2 or 3 each R_2 is the same as or different from any other R^2, n and r are each 0 or 1 but are not both zero simultaneously, q is 0 or 1 and t is an integer from 0 to 4, it being understood that the word "integer" as used herein includes zero.

As used above, the term "lower" usually indicates a group having not more than 5 carbon atoms. Examples of lower alkyl are methyl, ethyl, n-propyl, isopropyl and t-butyl. Examples of lower alkoxy are methoxy, ethoxy, n-propoxy, isopropoxy and t-butoxy. Examples of halogen are fluorine, chlorine and bromine.

The compounds of the invention are useful as herbicides for controlling and exterminating weeds without any unfavorable influence on the growth of crop plants.

It is of course desirable that herbicides should have high safety to crop plants. However, herbicides for post-emergence application contact not only the foliage of weeds but also the foiliage of crop plants so that the extermination of only the weeds is very difficult. In fact few herbicides of this type are commercially available.

It has now been found that the oximecarbamate derivatives (I) of the present invention can control and exterminate weeds efficiently without causing any chemical injury to crop plants such as soybean, cotton, sugar beet and wheat by post-emergence application. For instance, the compounds (I) can exterminate redroot pigweed (*Amaranthus retroflexus*), sunflower (*Helianthus annuus*), cocklebur (*Xanthium pennsylvanicum*), annual morningglory (*Ipomoea purpurea*), crabgrass (*Digitaria adscendens*), barnyard grass (*Echinochloa crus-galli*), etc. in the cotton or soybean field, and common lambsquarter (*Chenopodium album*), radish, black nightshade (*Solanum nigrum*), green foxtail (*Setaria viridis*), etc. in the sugar beet or wheat field with high safety to the crop plants, when applied after emergence of the weeds. Thus, they are useful as selective herbicides for post-emergence treatment in the culture of cotton, soybean, sugar beet or wheat.

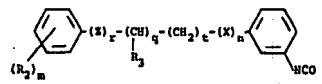
Furthermore, the compounds (I) show a herbicidal activity by soil treatment of paddy fields. For instance, their application to rice paddy fields can exterminate barnyard grass (*Echinochloa crus-galli*), pickerel weed (*Monochoria vaginalis*), false pimpernel (*Lindernia pyxidaria*), toothcup (*Rotala indica*), nutsedge sp. (*Cyperus difformis*), etc. without causing any chemical injury to rice plants.

While the oximecarbamate derivatives (I) are novel, there is known O-(N-phenylcarbamoyl) acetoxime (W. German patent 1,024,746; Control (a)). However, no herbicidal activity of this control compound (a) on foliage treatment has been described, and in fact, its herbicidal activity on foliage treatment is much inferior to that of the compounds (I).

The compounds are characteristic in having a substituent such as substituted phenoxy, substituted phenylthio, substituted phenylalkyloxy, substituted phenylalkylthio, substituted phenoxyalkyl, substituted phenylthioalkyl, substituted phenoxyalkyloxy or phenylthioalkyloxy at the m-position of the phenyl group in the O-(N-phenylcarbamoyl)oxime derivative. As will be shown hereinafter, the herbicidal activity of O-[N-{4-(2-fluorophenoxymethyl) phenyl} carbamoyl] acetoxime (Control (b)) or of O-[N-{4-(3-(4-chlorophenyl) propoxy) phenyl} carbamoyl] acetoxime (Control (c)) is much inferior to the herbicidal activity of the compounds (I).

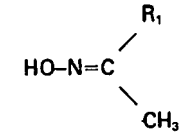
In general, the compounds (I) exhibit high selectivity to soybean, cotton, sugar beet and wheat. The selectivity is closely associated with their structure. For instance, O-[N-{3-(3-chlorophenoxymethyl)phenyl}carbamoyl]-acetoxime (Compound No. 21) shows selectivity to cotton and sugar beet. When the chlorine atom at the m-position is changed to a trifluoromethyl group, the resulting compound (Compound No. 32) shows selectivity to soybean and wheat losing selectivity to sugar beet and cotton. Further, when the methyl group in the dimethylacetoxime group of Compound No. 32 is replaced by a methoxy group, the resultant compound (Compound No. 33) shows selectivity to sugar beet and wheat losing selectivity to soybean. Furthermore, O-[N-{3-(3-chlorophenethyloxy) phenyl} carbamoyl] methoxyethanaloxime (Compound No. 103) shows selectivity only to wheat.

The compounds (I) are novel and can be produced, for instance, by reacting a phenylisocyanate derivative of the formula:



(II)

wherein R_2, R_3, X, Z, m, n, r, q and t are each as defined above, with an oxime derivative of the formula:



(III)

wherein R_1 is as defined above.

The reaction may be carried out in an inert organic solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, N,N-dimethylformamide, chloroform, carbon tetrachloride). The presence of a

tertiary amine (e.g. pyridine, triethylamine, diethylanaline) in the reaction system is advantageous for effecting the reaction efficiently. Usually, the oxime derivative (III) is employed in an equimolar to excess molar amounts, preferably in an equimolar to 1.5 fold molar excess, to the phenylisocyanate derivative (II).

The reaction is usually effected at a temperature from 0 to 100°C and sometimes under cooling or heating, and it is normally completed within about 10 hours. The reaction product can be recovered from the reaction mixture by a conventional separation procedure such as filtration or distillation. If necessary, the recovered product may be further purified, for instance, by recrystallization or column chromatography.

The phenylisocyanate derivative (II) and the oxime derivative (III) are known.

Practical and presently preferred embodiments of the preparation of the compounds (I) are illustratively shown in the following examples.

Example 1

To a solution of acetoxime (8.1 g) in benzene (100 ml), there was dropwise added a solution of m - (3, 4 - dichlorophenoxymethyl)phenylisocyanate (29.4 g) in benzene (50 ml) at 10 to 20°C. The mixture was stirred at the same temperature for 3 hours, and thereafter the solvent was removed. The residue was recrystallized from a mixture of benzene and tetrahydrofuran (5:1 by volume) to obtain 25.3 g of white needles (Compound No. 36). M.P., 79-81°C.

Elementary analysis: Calcd. for $C_{17}H_{16}Cl_2N_2O_3$: C, 55.59%; H, 4.40%; N, 7.63%; Cl, 19.30%. Found: C, 55.56%; H, 4.25%; N, 7.70%; Cl, 19.44%.

Example 2

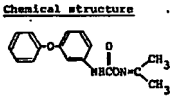
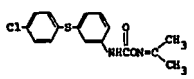
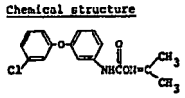
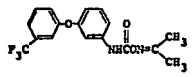
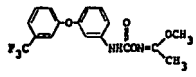
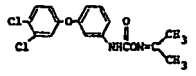
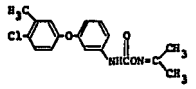
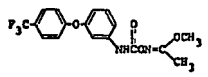
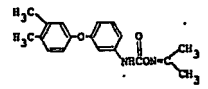
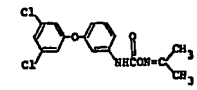
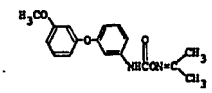
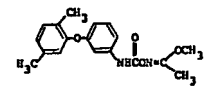
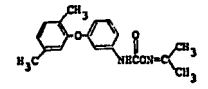
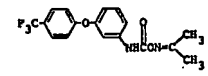
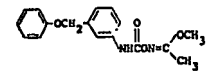
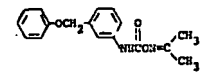
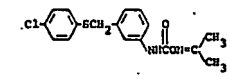
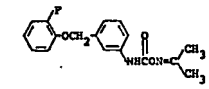
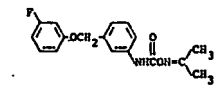
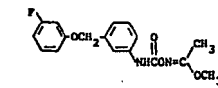
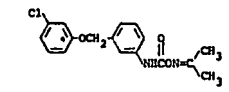
To a solution of methoxyethanaloxime (8.9 g) in toluene (150 ml), there was added triethylamine (0.2 g). To this solution, there was dropwise added a solution of m - (4 - tert - butylphenoxymethyl) phenylisocyanate (28.1 g) in toluene (60 ml) at 50-60°C. The mixture was stirred at the same temperature for 2 hours, and thereafter the solvent was removed. The oily substance obtained was purified by column chromatography (silica gel, 70-230 mesh) using a mixture of benzene and tetrahydrofuran (8:1 by volume) to obtain 16.7 g of an oily substance (Compound No. 27).

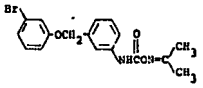
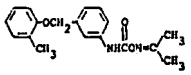
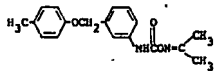
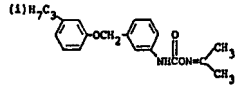
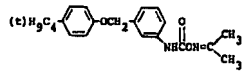
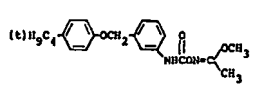
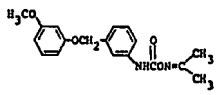
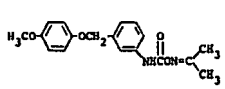
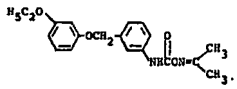
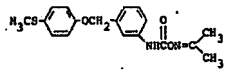
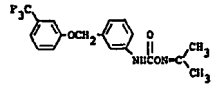
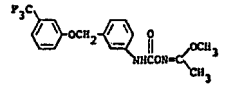
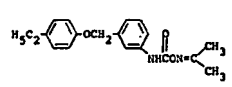
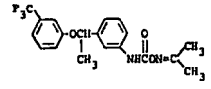
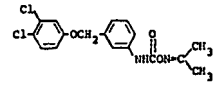
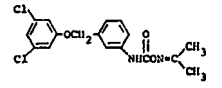
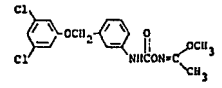
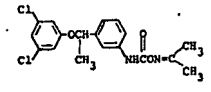
n_D^{25}: 1.5590.

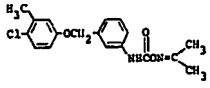
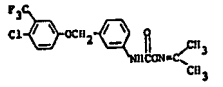
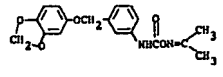
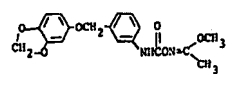
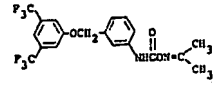
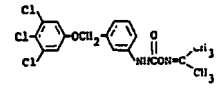
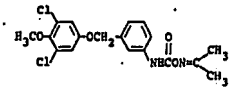
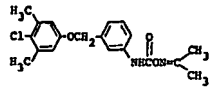
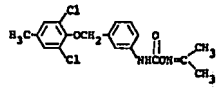
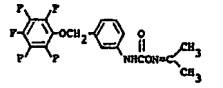
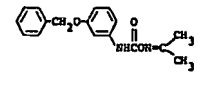
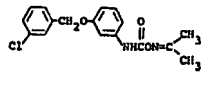
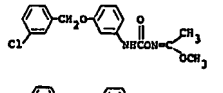
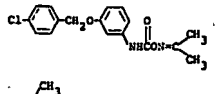
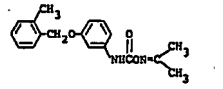
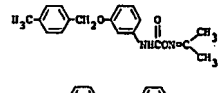
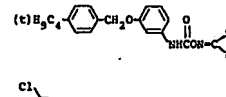
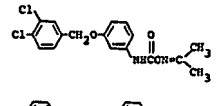
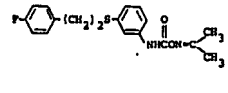
Elementary analysis: Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.07%; H, 7.09%; N, 7.56%. Found: C, 68.13%; H, 7.12%; N, 7.44%.

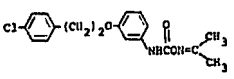
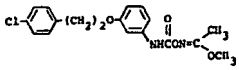
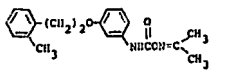
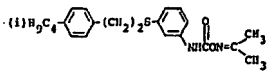
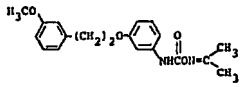
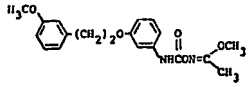
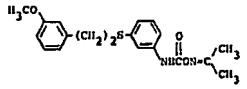
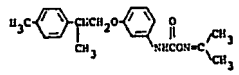
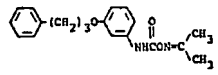
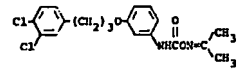
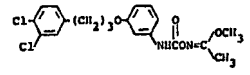
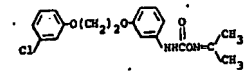
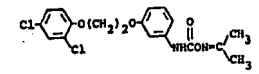
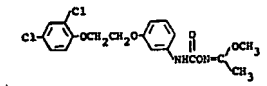
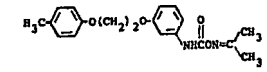
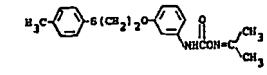
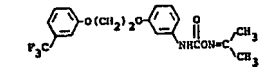
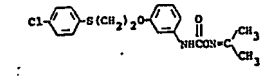
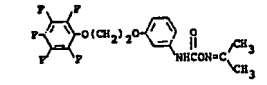
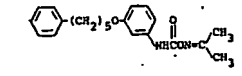
Some specific examples of the compound (I), which can be prepared in the same manner as above, are shown in Table 1 below but the compounds of the invention are not limitative to these examples.

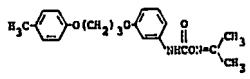
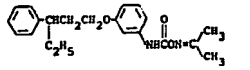
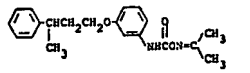
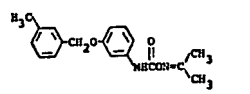
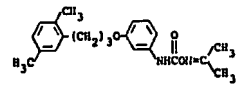
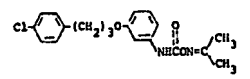
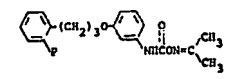
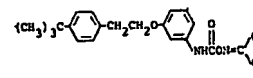
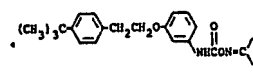
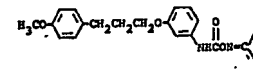
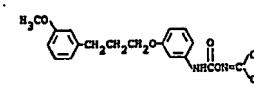
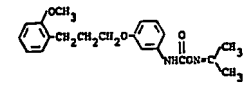
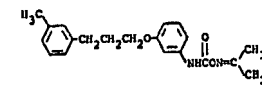
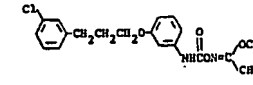
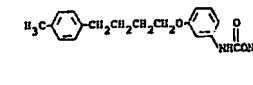
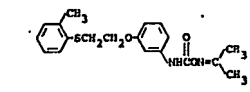
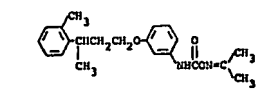
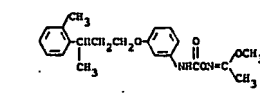
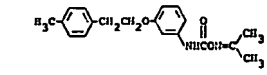
Table 1

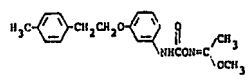
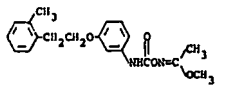
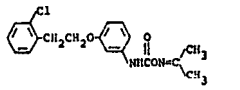
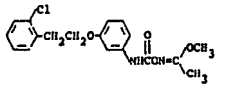
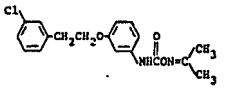
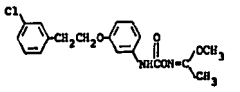
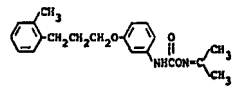
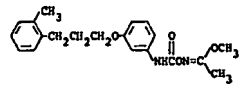
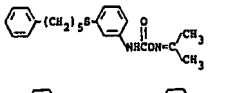
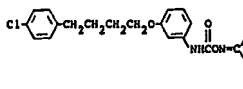
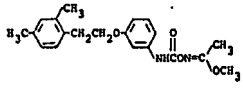
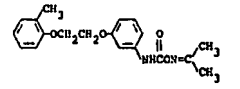
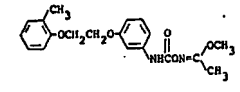
Compound No.	Chemical structure	Melting point or refractive index
1		M.P., 119-120°C
2		M.P., 77-79°C
3		M.P., 71-75°C
4		n_D^{23} 1.5445
5		n_D^{23} 1.5312
6		$n_D^{25.5}$ 1.5918
7		$n_D^{25.5}$ 1.5882
8		M.P., 58-60°C
9		M.P., 119-121°C
10		M.P., 107-108°C
11		M.P., 59-60°C
12		n_D^{22} 1.5735
13		M.P., 95.5-96.5
14		M.P., 80-82°C
15		n_D^{24} 1.5671
16		M.P., 47.5-49.5°C
17		M.P., 89-91°C
18		M.P., 97-98°C
19		M.P., 10-13°C
20		n_D^{26} 1.5691
21		M.P., 59-61°C

Compound No.	Chemical structure	Melting point or refractive index
22		M.P., 76-77°C
23		M.P., 76-77°C
24		n_D^{24} 1.5821
25		$n_D^{22.5}$ 1.5478
26		M.P., 98-100°C
27		n_D^{25} 1.5590
28		n_D^{24} 1.5771
29		n_D^{21} 1.5800
30		n_D^{23} 1.5645
31		M.P., 81-82°C
32		n_D^{27} 1.5496
33		n_D^{24} 1.5852
34		n_D^{24} 1.5793
35		$n_D^{25.5}$ 1.5341
36		M.P., 79-81°C
37		M.P., 36-37°C
38		n_D^{25} 1.5778
39		$n_D^{27.5}$ 1.5750

Compound No.	Chemical structure	Melting point or refractive index
40		M.P., 89-90°C
41		M.P., 83-85°C
42		M.P., 84-86°C
43		M.P., 45-50°C
44		$n_D^{25.5}$ 1.5739
45		n_D^{25} 1.5891
46		M.P., 83-84°C
47		M.P., 115-117°C
48		M.P., 110-112°C
49		$n_D^{25.5}$ 1.5305
50		M.P., 116-117°C
51		M.P., 77-78°C
52		M.P., 79.5-81°C
53		M.P., 128-129°C
54		M.P., 120-122°C
55		M.P., 108-110°C
56		M.P., 126-127°C
57		$n_D^{22.5}$ 1.5919
58		n_D^{24} 1.5975

Compound No.	Chemical structure	Melting point or refractive index
59		n_D^{27} 1.5770
60		M.P., 99-100°C
61		M.P., 95-96°C
62		n_D^{22} 1.5845
63		n_D^{27} 1.5689
64		M.P., 78-82°C
65		$n_D^{23.5}$ 1.5970
66		$n_D^{27.5}$ 1.5587
67		$n_D^{26.5}$ 1.5593
68		n_D^{30} 1.5861
69		n_D^{30} 1.5762
70		M.P., 87-89°C
71		M.P., 89.5-91°C
72		M.P., 54-56°C
73		M.P., 89.5-91°C
74		M.P., 64-66°C
75		M.P., 106.5-107.5°C
76		M.P., 55-57°C
77		n_D^{28} 1.5233
78		n_D^{26} 1.5590

Compound No.	Chemical structure	Melting point or refractive index
79		M.P., 163-166°C
80		M.P., 84-86.5°C
81		$n_D^{24.5}$ 1.5608
82		$n_D^{24.5}$ 1.5786
83		$n_D^{25.5}$ 1.5675
84		$n_D^{24.5}$ 1.5770
85		$n_D^{24.5}$ 1.5556
86		M.P., 98-99.5°C
87		n_D^{30} 1.5515
88		M.P., 58-60°C
89		$n_D^{29.5}$ 1.5666
90		n_D^{27} 1.5516
91		n_D^{28} 1.5742
92		n_D^{27} 1.5632
93		$n_D^{29.5}$ 1.5649
94		M.P., 53-55°C
95		n_D^{21} 1.5569
96		n_D^{21} 1.5618
97		$n_D^{29.5}$ 1.5599

Compound No.	Chemical structure	Melting point or refractive index
98		M.P., 61-64°C
99		M.P., 68-70°C
100		M.P., 89-90°C
101		$n_D^{24.5}$ 1.5739
102		n_D^{27} 1.5648
103		M.P., 71-72.5°C
104		$n_D^{29.5}$ 1.5592
105		n_D^{21} 1.5708
106		n_D^{29} 1.5950
107		M.P., 65-66°C
108		$n_D^{26.5}$ 1.5605
109		M.P., 102-104°C
110		M.P., 81-83°C

In the practical usage of the compounds (I), they may be applied neat or in the form of any composition such as wettable powders, emulsifiable concentrates, granules, fine granules or dusts.

In producing such compositions form, a solid or liquid carrier may be used. As examples of solid carriers, there may be given mineral powders (e.g. kaolin, bentonite, clay, montmorillonite, talc, diatomaceous earth, mica, vermiculite, gypsum, calcium carbonate, apatite), vegetable powders (e.g. soybean powder, flour, wooden powder, tobacco powder, starch, crystalline cellulose), high molecular weight compounds (e.g. petroleum resin, polyvinyl chloride, dammar gum, ketone resin), alumina, wax and the like.

Examples of liquid carriers are alcohols (e.g. methanol, ethanol, ethylene glycol, benzyl alcohol), aromatic hydrocarbons (e.g. toluene, benzene, xylene, methylnaphthalene), halogenated hydrocarbons (e.g. chloroform, carbon tetrachloride, monochlorobenzene), ethers (e.g. dioxane, tetrahydrofuran), ketones (e.g. acetone, methyl ethyl ketone, cyclohexanone), esters (e.g. ethyl acetate, butyl acetate, ethylene glycol acetate), acid amides (e.g. dimethylformamide), nitriles (e.g. acetonitrile), ether alcohols (e.g. ethylene glycol ethyl ether), water and the like.

A surface active agent may be used for emulsification dispersion or spreading and may be any of the non-ionic, anionic, cationic and amphoteric type of agents. Examples of the surface active agent include polyoxyethylene alkyl ethers, polyoxyethylene alkylaryl ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, oxyethylene polymers, oxypropylene polymers, polyoxyethylene alkyl phosphates, fatty acid salts, alkyl sulfates, alkyl sulfonates, alkylaryl sulfonates, alkyl phosphates, quaternary ammonium salts and the like. But, the surface active agent is not of course limited to these compounds. And, if necessary, gelatin, casein, sodium alginate, starch, agar, polyvinyl alcohol or the like may be used as an auxiliary agent.

In the preparation of a herbicidal composition, the content of the compound (I) may be from 1 to 95% by weight, preferably from 1 to 80% by weight.

Practical embodiments of the herbicidal composition according to the invention are illustratively shown in the following examples wherein parts and % are by weight.

Preparation Example 1

Eighty parts of Compound No. 36, 5 parts of polyoxyethylene alkylaryl ether and 15 parts of synthetic silicon oxide hydrate are well mixed while being powdered to obtain a wettable powder.

Preparation Example 2

Thirty parts of Compound No. 21, 7 parts or polyoxyethylene alkylaryl ether, 3 parts of alkylaryl sulfonate and 60 parts of xylene are well mixed to obtain an emulsifiable concentrate.

Preparation Example 3

One part of Compound No. 69, 1 part of white carbon, 5 parts of ligninsulfonate and 93 parts of clay are well mixed while being powdered. The mixture is then well kneaded with water, granulated and dried to obtain a granule.

Preparation Example 4

Fourty parts of bentonite, 5 parts of ligninsulfonate and 55 parts of clay are well mixed while being powdered. The mixture is then well kneaded with water, granulated and dried to obtain a granule containing no active ingredient. The granule is then impregnated with 5 parts of Compound No. 32 to obtain a granule.

Preparation Example 5

Three parts of Compound No. 27, 0.5 part of isopropyl phosphate, 66.5 parts of clay and 30 parts of talc are well mixed while being powdered to obtain a dust.

The compounds (I) of the invention may be used together with other herbicides to improve their activity as herbicides, and in some cases, a synergistic effect can be expected. As the other herbicides, there

may be given phenoxy series herbicides such as 2, 4 - dichlorophenoxyacetic acid, 2 - methyl - 4 - chlorophenoxyacetic acid and 2, 4 - dichlorophenoxybutyric acid (including esters and salts thereof); diphenyl ether series herbicides such as 2, 4 - dichlorophenyl - 4' - nitrophenyl ether, 2, 4, 6 - trichlorophenyl - 4' - nitrophenyl ether, 2, 4 - dichloro - 3' - methoxy - 4' - nitrophenyl ether, 2, 4 - dichlorophenyl - 3' - methoxycarbonyl - 4' - nitrophenyl ether and 2 - chloro - 4 - trifluoromethylphenyl - 3' - hydroxycarbonyl - 4' - nitrophenyl ether; triazine series herbicides such as 2 - chloro - 4, 6 - bisethylamino - 1, 3, 5 - triazine, 2 - chloro - 4 - ethylamino - 6 - isopropylamino - 1, 3, 5 - triazine, 2 - methylthio - 4, 6 - bisethylamino - 1, 3, 5 - triazine, 2 - methylthio - 4, 6 - bisisopropylamino - 1, 3, 5 - triazine, 4 - amino - 3 - methyl - 6 - phenyl - 1, 2, 4 - triazine - 5 (4H) - one and 4 - amino - 6 - tert - butyl - 3 - methylthio - 1, 2, 4 - triazine - 5 (4H) - one; urea series herbicides such as 3 - (3, 4 - dichlorophenyl) - 1, 1 - dimethylurea, 3 - (3, 4 - dichlorophenyl) - 1 - methoxy - 1 - methylurea, 3 - (3 - chloro - 4 - difluorochloromethylthiophenyl) - 1, 1 - dimethylurea, 3 - [4 - (4 - chlorophenoxy)phenyl] - 1, 1 - dimethylurea and 3 - (α, α, α - trifluoro - m - tolyl) - 1, 1 - dimethylurea; carbamate series herbicides such as isopropyl - N - (3 - chlorophenyl)carbamate, methyl - N - (3, 4 - dichlorophenyl) carbamate and 4 - chloro - 2 - butynyl - m - chlorocarbanilate; thiolcarbamate series herbicides such as S - (4 - chlorobenzyl) - N, N - diethylthiolcarbamate, S - ethyl - N, N - hexamethylenethiolcarbamate and S - ethyl dipropylthiolcarbamate; acid anilide series herbicides such as 3, 4 - dichloropropionanilide, N - methoxymethyl - 2, 6 - diethyl - 2 - chloroacetanilide and 2 - chloro - 2', 6' - diethyl - N - (butoxymethyl)acetanilide; uracil series herbicides such as 5 - bromo - 3 - sec - butyl - 6 - methyluracil and 3 - cyclohexyl - 5, 6 - trimethyleneuracil; pyridinium salt series herbicides such as 1, 1' - dimethyl - 4, 4' - bispyridinium dichloride; phosphorus series herbicides such as N - (phosphonomethyl)glycine, O - methyl - O - (2 - nitro - 5 - methylphenyl) - N - sec - butylphosphoroamidothioate and O - ethyl - O - (2 - nitro - 4 - methylphenyl) - N - isopropyl - phosphoroamidothioate; toluidine series herbicides such as α, α, α - trifluoro - 2, 6 - dinitro - N, N - dipropyl - p - toluidine, N - (cyclopropylmethyl) - α, α, α - trifluoro - 2, 6 - dinitro - N - propyl - p - toluidine; N - sec - butyl - 4 - tert - butyl - 2, 6 - dinitroaniline; 3, 5 - dinitro - 4 - N, N - dipropylaminosulfanylamide; 5 - tert - butyl - 3 - (2, 4 - dichloro - 5 - isopropoxyphenyl) - 1, 3, 4 - oxadiazolin - 2 - one; 3 - isopropyl - 1H - 2, 1, 3 - benzothiadiazine(4) - 3H - one - 2, 2 - dioxide (including salts thereof); α - (β - naphthoxy)propionanilide; 2 - (α - naphthoxy) - N, N - diethylpropionamide; 3 - amino - 2, 5 - dichlorobenzoic acid; 2 - sec - butyl - 4, 6 - dinitrophenol; N - 1 - naphthylphthalamic acid; 5 - amino - 4 - chloro - 2 - phenyl - 3 (2H) - pyridazine and the like. But, the herbicides are not of course limited to these examples.

The herbicides of the invention may be applied together with fungicides, pyrethroid series insecticides, other insecticides, plant growth regulators, fertilizers, etc.

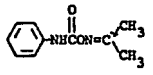
The dosage rate of the compounds (I) depends upon their kinds, the sorts of cultivated plants, the method of application, etc. Generally, however, the dosage rate is from 2 to 200 grams, preferably from 5 to 50 grams, of the active ingredient per are.

The application of the compounds (I) as herbicides will be illustrated in the following Examples wherein the phytotoxicity to cultivated plants and the herbicidal activity on weeds were evaluated as follows: the aereal parts of the test plants were cut off and weighed (fresh weight); the percentage of the fresh weight of the treated plant to that of the untreated plant was calculated with the latter fresh weight taken as 100; and the crop damage and the herbicidal activity were evaluated by the standard given in the table below. The rating values of phytotoxicity, 0 and 1, and those of herbicidal effect, 5 and 4, are generally regarded as satisfactory to protect cultivated plants and to control weeds, respectively. The rating values in the paddy rice test alone were calculated from the dry weight of plant.

Rating value	Fresh weight (percentage to untreated plot)	
	Cultivated plant	Weed
5	0 - 39	0
4	40 - 59	1 - 10
3	60 - 79	11 - 20
2	80 - 89	21 - 40
1	90 - 99	41 - 60
0	100	61 - 100

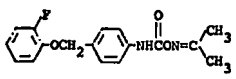
The following control compounds were used in the Examples.

Control (a)



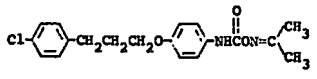
(M.P. 143-145°C)

Control (b)



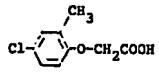
(M.P., 135-136°C)

Control (c)

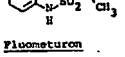


(M.P., 120-121°C)

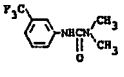
MCP



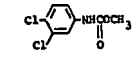
Bentazon



Fluometuron



Swep



Example I (Paddy race test)

Wagner's pots (1/5000 are) were each filled with 1.5 kg of paddy field soil containing the seeds of weeds and kept under flooded conditions. The seedlings of rice plant at a 3-leaf stage were transplanted thereto, and after the seeds of barnyard grass were sowed therein, the seedlings were grown for 15 days in a green-house. Thereafter, the required amount of the wettable powder of each test compound was diluted with water and applied to the soil under flooded conditions. Twenty-five days after the application, the evaluation of herbicidal activity and phytotoxicity was made on the rice plants and barnyard grass as well as broad-leaved weeds (e.g. pickerel weed (*Monochoria vaginalis*), false pimpernel (*Lindernia pyxidaria*), toothcup (*Rotala indica*) and nutsedge sp. (*Cyperus difformis*). The results are shown in Table 2.

Table 2

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barnyard grass	Broad-leaved weed	Nutsedge sp.
1	20	0	4	4	5
2	20	0	4	5	5
3	20	0	5	5	5
	10	0	4	5	4
4	20	0	4	5	5
5	20	0	4	4	4
6	20	0	-	5	4
7	20	0	4	5	5
8	20	0	-	5	5
9	20	0	-	5	4
10	20	0	4	5	5
11	20	0	-	5	5
12	20	0	4	5	5
13	20	0	-	5	5
14	20	0	5	5	5
15	20	0	-	5	5
16	20	0	4	5	5
17	20	0	5	5	4
18	20	0	5	5	5
	10	0	4	5	5
19	20	0	5	5	5
	10	0	5	5	5
20	20	0	5	5	5
	10	0	5	5	5
21	20	0	5	5	5
	10	0	4	5	5
22	20	0	5	5	5
	10	0	4	5	5
23	20	0	-	5	5
24	20	0	4	4	5
25	20	1	5	5	5
26	20	0	5	5	5
	10	0	4	5	5
27	20	0	5	5	5
28	20	0	4	5	4
29	20	0	4	5	5
30	20	0	-	5	5
31	20	0	-	4	4
32	20	0	5	5	5
	10	0	5	5	5
33	20	0	4	5	5
35	20	0	5	5	5
	10	0	4	5	5
36	20	0	5	5	5
	10	0	4	5	5
37	20	0	5	5	5
	10	0	5	5	5
38	20	0	5	5	5
	10	0	4	5	5
39	20	0	4	5	4
40	20	0	4	5	5
	10	0	-	5	4

(Continued)

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barnyard grass	Broad-leaved weed	Nutsedge sp.
41	20	0	5	5	5
	10	0	4	5	5
42	20	0	-	5	4
43	20	0	-	4	4
44	20	0	5	5	5
45	20	0	5	5	5
	10	0	4	5	5
46	20	0	4	5	5
47	20	0	-	5	5
48	20	0	4	5	4
49	20	0	5	5	5
50	20	0	5	5	5
51	20	0	5	5	5
	10	0	4	5	5
52	20	0	5	5	5
53	20	0	4	5	5
54	20	0	4	5	5
55	20	0	5	5	5
56	20	0	5	5	5
	10	0	4	5	5
57	20	0	5	5	5
	10	0	5	5	5
58	20	0	-	5	4
59	20	0	5	5	5
	10	0	4	5	5
60	20	0	5	5	5
61	20	0	-	5	5
62	20	0	-	5	5
63	20	0	4	4	4
64	20	0	4	5	5
65	20	0	4	5	5
66	20	0	5	5	5
67	20	0	-	4	5
68	20	0	-	5	5
69	20	0	4	5	5
70	20	0	4	5	4
71	20	0	4	5	5
72	20	0	-	5	4
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75	20	0	4	5	4
76	20	0	-	4	4
77	20	0	4	5	5
78	20	0	-	5	4
79	20	0	-	4	4
80	20	0	-	5	5
81	20	0	4	5	5
82	20	0	4	5	4
83	20	0	4	5	5
84	20	0	5	5	5
	10	0	4	5	5
85	20	1	5	5	5
	10	0	5	5	5
86	20	0	4	5	4
87	20	0	4	5	5
88	20	0	-	5	4
89	20	0	-	5	5
90	20	0	-	5	5
91	20	0	-	5	4
92	20	0	5	5	5
	10	0	4	5	5
93	20	0	-	5	5
94	20	0	-	5	5
95	20	0	4	5	5
96	20	0	4	5	5
97	20	0	4	5	5
	10	0	-	5	5
98	20	0	5	5	5
	10	0	4	5	5
99	20	0	4	5	5
	10	0	4	5	5
100	20	0	4	5	5
101	20	0	4	5	5
	10	0	-	5	5
102	20	0	4	5	5

(Continued)

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barnyard grass	Broad-leaved weed	Nutsedge sp.
103	20	0	5	5	5
	10	0	4	5	5
104	20	0	4	5	5
105	20	0	-	5	5
106	20	0	-	5	4
107	20	0	-	5	4
108	20	0	4	5	5
109	20	0	4	5	5
110	20	0	-	5	4
Control (a)	40	0	0	2	1
	20	0	0	1	0
Control (b)	40	1	0	3	2
	20	0	0	2	0
Control (c)	40	1	1	3	3
	20	1	0	1	2
MCP	20	3	4	5	5
	10	3	3	5	5

Example II (Post-emergence application test (weeds))

Plastic trays (35 cm x 25 cm x 10 cm (high)) were filled with upland field soil, and the seeds of redroot pigweed, common lambsquarter, radish, sunflower, cocklebur, annual morningglory, black nightshade, large crabgrass, barnyard grass and green foxtail were separately sowed in the trays and grown for 3 weeks in a green-house. The required amount of the test compound was sprayed to the foliage of the test plants over the top by means of a small hand sprayer. After the spraying, the test plants were grown for further 3 weeks in the green-house, and herbicidal activity was examined. The results are shown in Table 3. In the above foliar application, the test compounds were each formulated into an emulsifiable concentrate, and the required amount of the emulsifiable concentrate was dispersed in water for application at a spray volume of 5 liters per are and applied with the addition of a wetting agent. At the time of application, the weeds were in a 2- to 4-leaf stage and 2 to 12 cm in height although there was some difference depending upon the kind of weed.

Table 3

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity									
		Redroot pigweed	Common lambs-quarter	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barnyard grass	Green foxtail
3	20	5	5	5	5	5	5	5	4	4	4
4	20	5	5	5	5	5	4	5	4	-	4
6	20	5	5	5	5	4	5	5	-	-	4
7	20	5	5	5	5	5	5	5	-	4	4
8	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	4	-	4
10	20	5	5	5	5	4	5	5	-	4	4
12	20	5	5	5	5	5	5	5	-	-	4
14	20	5	5	5	5	5	5	5	-	5	-
15	20	5	5	5	5	5	5	5	4	5	4
16	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	-	4
17	20	5	5	5	5	5	5	5	5	4	5
18	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	4	5
19	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
20	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4
21	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	5	4
22	20	5	5	5	5	5	5	5	5	4	5
23	20	5	5	5	5	5	4	5	4	4	4
26	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4
27	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	4	5	4	5	-	4	4
29	20	5	5	5	5	5	5	5	4	4	4
32	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	4
33	20	5	5	5	5	5	5	5	4	5	4
	10	5	5	5	5	5	5	5	4	4	4
35	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	5
36	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	4	4	4
37	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	5
38	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	4	4	4
40	20	5	5	5	5	5	5	5	4	4	4
41	20	5	5	5	5	5	5	5	4	4	5
44	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	-	4
45	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	4	4	4
46	20	5	5	5	5	5	5	5	4	-	4
49	20	5	5	5	5	5	5	5	4	5	5
51	20	5	5	5	4	4	5	5	5	4	4
52	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4

(Continued)

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity									
		Redroot pigweed	Common lambs-quarter	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barnyard grass	Green foxtail
53	20	5	5	5	5	5	5	5	4	5	4
54	20	5	5	5	5	5	5	5	4	4	5
55	20	5	5	5	5	5	5	5	4	5	5
56	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	-	5
57	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	4	4	4
58	20	5	5	5	5	5	4	5	4	-	4
59	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	5
60	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	4	-	4
61	20	5	5	5	5	5	5	5	-	5	5
63	20	5	5	5	5	5	5	5	4	4	5
64	20	5	5	5	5	5	5	5	4	5	4
67	20	5	5	5	5	5	5	5	4	4	5
69	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4
70	20	5	5	5	5	5	5	5	-	4	5
71	20	5	5	5	5	5	5	5	4	4	5
72	20	5	5	5	5	5	5	5	4	5	5
75	20	5	5	5	5	5	5	5	-	4	-
76	20	5	5	5	5	5	4	5	-	4	4
78	20	5	5	5	5	5	5	5	-	-	4
79	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	-	4	4
80	20	5	5	5	5	5	5	5	-	4	4
81	20	5	5	5	5	5	5	5	4	4	5
83	20	5	5	5	5	5	5	5	4	4	4
84	20	5	5	5	5	5	5	5	-	4	5
85	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	-	5
87	20	5	5	5	5	5	4	5	-	4	4
91	20	5	5	5	5	5	5	5	4	-	5
92	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	3	3
94	20	5	5	5	5	5	5	5	-	-	4
95	20	5	5	5	5	5	5	5	4	-	4
96	20	5	5	5	5	5	5	5	4	4	-
97	20	5	5	5	5	5	5	5	4	5	5
98	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	5
99	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
100	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	-	4
101	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	-	4	4
102	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	-	4	-
103	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	5	5
104	20	5	5	5	5	5	5	5	4	4	-
105	20	5	5	5	5	5	5	5	-	4	4
108	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	4	5	4	-	4
110	20	5	5	5	5	5	5	5	4	4	4
Control (a)	40	1	0	0	0	0	0	1	0	0	0
	20	0	0	0	0	0	0	0	0	0	0
Control (b)	40	0	0	1	0	0	0	0	0	0	0
	20	0	0	0	0	0	0	0	0	0	0
Control (c)	40	0	2	2	0	0	0	3	0	0	1
	20	0	0	0	0	0	0	1	0	0	0
Bentazon	20	3	5	5	5	5	4	5	1	2	0
	10	3	5	5	5	5	2	5	0	1	0
Fluo-meturon	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
Swep	20	5	5	5	5	5	3	5	5	5	4
	10	5	4	4	5	5	3	3	2	4	4

Example III (Post-emergence application test (cultivated plants))

Wagner's pots (1/5000 are) were each filled with upland field soil, and the seeds of soybean, cotton, sugar beet and wheat were sowed in the pots and grown for 3 weeks in a green-house. The required amount of the test compound was sprayed to the foliage of the test plants over the top by means of a small hand sprayer. After the spraying, the test plants were grown for further 3 weeks in the green-house, and phytotoxity was examined. In the above foliar application, the test compounds were each formulated into an emulsifiable concentrate, and the required amount of the emulsifiable concentrate was

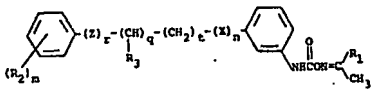
dispersed in water for application with the addition of wetting agent. At the time of application, soybean was in the second trifoliate stage, cotton in the 1-leaf stage, sugar beet in the 2-leaf stage and wheat in the 2-leaf stage. The results are shown in Table 4.

Table 4

Compound No.	Dosage (weight of active ingredient, g/are)	Phytotoxicity			
		Soybean	Cotton	Sugar beet	Wheat
3	20	1	-	-	1
7	20	1	-	-	-
8	20	-	-	-	1
	10	-	-	-	0
36	20	1	-	-	0
	10	1	-	-	0
37	20	-	-	1	1
	10	-	-	1	0
38	20	1	-	-	-
	10	1	-	-	-
41	20	1	-	-	0
44	20	1	-	-	1
	10	1	-	-	0
45	20	-	-	-	1
	10	-	-	-	0
46	20	1	-	1	0
49	20	0	1	-	-
52	20	1	1	-	-
	10	0	0	-	-
56	20	0	0	-	1
	10	0	0	-	0
61	20	1	-	-	0
	10	1	-	-	0
60	20	1	1	-	1
	10	0	1	-	0
69	20	1	-	-	-
	10	1	-	-	-
71	20	0	1	-	-
76	20	1	0	-	-
79	20	0	-	-	-
81	20	1	-	0	0
84	20	1	-	-	-
85	20	0	-	-	-
98	20	1	0	-	-
	10	0	0	-	-
99	20	-	-	1	0
	10	-	-	0	0
101	20	1	-	1	-
	10	0	-	1	-
102	20	1	-	1	-
	10	0	-	0	-
103	20	-	-	-	1
	10	-	-	-	0
Bentazon	20	0	-	5	-
	10	0	-	5	-
Fluometuron	20	-	2	-	-
	10	-	1	-	-
Swep	20	-	-	5	3
	10	-	-	5	1

CLAIMS

1. A compound of the formula:



wherein R_1 is methyl or methoxy, R_2 is lower alkyl, lower alkoxy, methylenedioxy, methylthio, halogen or trifluoromethyl, R_3 is hydrogen, methyl or ethyl, X and Z are each oxygen or sulfur, m is an integer from 0 to 5 when R_2 is fluorine or an integer from 0 to 3 when R_2 is other than fluorine when m is 2 or 3 each R_2 is the same as or different from any other R^2, n and r are each 0 or 1 but are not both zero, simultaneously, q is 0 or 1 and t is an integer from 0 to 4.

2. A compound as claimed in claim 1, wherein R_1 is methoxy, R_2 is lower alkyl, lower alkoxy or halogen, X is oxygen, m is 0, 1 or 2, n is 1, r is 0, q is 1 and t is an integer from 1 to 4.

3. A compound as claimed in claim 1, wherein R_2 is lower alkyl, lower alkoxy, halogen or trifluoromethyl, R_3 is hydrogen or methyl, Z is oxygen, m is an integer from 0 to 3, n is 0, r is 1, q is 1 and t is 0.

4. Any one of compounds 1 to 110 as hereinbefore defined.

5. O-[N-{3-(3-chlorophenoxymethyl) phenyl} carbamoyl] acetoxime.

6. O-[N-{3-(3-trifluoromethylphenoxymethyl) phenyl} carbamoyl] acetoxime.

7. O-[N-{3-(3-trifluoromethylphenoxymethyl) phenyl} carbamoyl] methoxyethanaloxime.

8. O-[N-{3-(3,4-dichlorophenoxymethyl) phenyl} carbamoyl] acetoxime.

9. O-[N-{3-(3,5-dichlorophenoxymethyl) phenyl} carbamoyl] acetoxime.

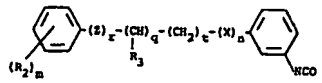
10. O-[N-{3-(3,4-dichlorophenyl-3-propyloxy) phenyl} carbamoyl] methoxyethanaloxime.

11. O-[N-{3-(4-methylphenethyloxy) phenyl} carbamoyl] methoxyethanaloxime.

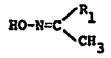
12. O-[N-{3-(3-chlorophenethyloxy) phenyl} carbamoyl] methoxyethanaloxime.

13. O-[N-{3-(4-tert-butylphenyloxymethyl) phenyl} carbamoyl] methoxyethanaloxime.

14. A process for preparing a compound as claimed in claim 1, which comprises reacting a compound of the formula:



with a compound of the formula:



wherein R_1, R_2, R_3, X, Z, m, n, q, r and t are each as defined in claim 1.

15. A compound as claimed in claim 1 when prepared by a process as claimed in claim 14.

16. A herbicidal composition which comprises a compound as claimed in any one of claims 1 to 13 or claim 15, together with a carrier.

17. A composition as claimed in claim 16, in the form of a wettable powder, an emulsifiable concentrate, granules, fine granules, or a dust.

18. A method of combating weeds, which method comprises contacting the weeds with a compound as claimed in any one of claims 1 to 13 or with a composition as claimed in claim 16 or 17.

19. A method of selectively combating weeds in the cultivation of soybean, cotton, sugar beet or wheat, which comprises applying a compound as claimed in any one of claims 1 to 13 or a composition as claimed in claim 16 or 17, to the area wherein the soybean, cotton, sugar beet or wheat is cultivated.

20. Use of the compound according to claim 1 as a herbicide.

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